Names:			
Chem 22	27/ Dr	Rusay	

Carboxylic Acid Derivatives: Nucleophilic Acyl Substitutions

1. Each of the following reactions involves nucleophilic substitution at an acyl carbon (carbonyl of a carboxylic acid or derivative) by way of a tetrahedral addition intermediate. Complete the separate table which follow the reactions indicating the two products that are formed.

	Product 1	Product 2
А		
В		
С		
D		
E		
F		
G		
Н		
I		
J		
К		
L		
M		
N		

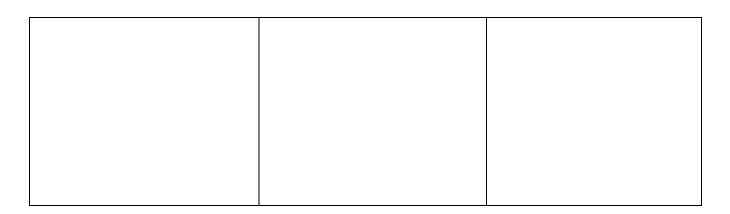
2. a. In the following case, predict which of the two competing reactions will be faster? Briefly explain your choice.

$$\begin{array}{c|c} O \\ (CH_3)_2CH-C-NH \\ O \\ \end{array} \begin{array}{c|c} A \\ (CH_3)_2CHCO_2H \\ \end{array} \begin{array}{c|c} O \\ N \\ \end{array} \begin{array}{c|c} (CH_3)_2CHCO_2H \\ \end{array} \begin{array}{c|c} O \\ N \\ \end{array} \begin{array}{c|c} O \\ \end{array} \begin{array}{c|c} O \\ N \\ \end{array} \begin{array}{c|c} O \\ O \\ H \\ H \end{array}$$

3. The ester shown is labeled with oxygen-18 as indicated ($^*O=^{18}O$). Provide a mechanism consistent with the labeling results shown when the ester is hydrolyzed in unlabeled water at pH = 2. Use arrows to show electron movement and show all intermediates.

$$\begin{array}{c}
O \\
\parallel \\
C \\
O \\
\end{array}
\begin{array}{c}
CH(CH_3)_2 \\
\hline
\Delta
\end{array}
\begin{array}{c}
O \\
\parallel \\
OH \\
+ H-O-CH_2CH_3
\end{array}$$

4.	Compound A, $C_{12}H_{16}O_2$, exhibited a strong absorption in the IR spectrum at 1715 cm ⁻¹ .
	Treatment of A with NaOH/H ₂ O gave a neutral compound B and a sodium salt that after
	acidification gave compound C. B exhibited strong broad absorption in the IR spectrum at 3333
	cm ⁻¹ and could be oxidized with aqueous chromic acid (Na ₂ Cr ₂ O ₇ /H ₂ SO ₄ /H ₂ O) to 2-
	methylbutanoic acid. C exhibited absorption in the IR spectrum at 1681 cm ⁻¹ and a very broad
	band over the range 2500-3500 cm $^{-1}$. The ¹ H NMR spectrum of C exhibited absorption at d 7.1-
	8.5 (m, 5H) and 12.70 (s 1H). Provide structures for A , B , and C .



- 5. BOC, Benzyloxychloroformate (BO₂C-Cl), PhCH₂OCCl, is a very important and widely used reagent applied to the synthesis of peptides and proteins as a protective group for the amino groups of aminoacids.
 - a. Show how BO_2C -Cl could be synthesized from phosgene.

b. Give the structure of the product from the reaction of $\rm BO_2C\text{-}Cl$ with the amino acid glycine, $\rm H_2NCH_2CO_2H$.

6. Dacron is a polyester formed by transesterification of dimethyl terephthalate with ethylene glycol to give a long-chain polymer molecule. Provide a partial structure of Dacron that shows two of the repeating units of the polymer (Use 2 molecules of each of the monomers below

$$H_3CO_2C$$
 CO_2CH_3 CO_2CH_3 ethylene glycol